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DETERMINATION OF THE SUSCEPTIBILITY TO ACIDIFICATION OF POORLY BUFFERED SURFACE WATERS

March 1979

Ministry
of the
Environment

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Ref. 72834

DETERMINATION OF THE SUSCEPTIBILITY TO ACIDIFICATION OF POORLY BUFFERED SURFACE WATERS

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M9W 5L1

March, 1979

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PREFACE

In January 1979, scientists from the Department of the Environment, Ontario Ministry of the Environment, Ontario Ministry of Natural Resources and the University of Toronto met at Sundridge, Ontario to discuss programs in Ontario dealing with the effects of long range transport of atmospheric pollutants.

A need for the development of a data base which would allow a) assessment of the effect of acidic precipitation on the lakes and rivers of the Canadian Shield and b) prediction of future effects of the acidity of precipitation was identified. It was recognized that existing data bases were either too small to make generalized assessments or of inadequate precision and/or accuracy to be of any significant use in this regard. Furthermore, it was recognized that the sampling and analytical techniques required for the collection of this data were very exacting due to the dilute nature of the waters of interest.

This manual was prepared for the use of personnel involved in water survey programs. It is designed to provide an introduction to the problem and a guide to the most appropriate field methods.

1.1 INTRODUCTION

The acidification of surface waters due to the input of "acidic rain" has occurred in the last fifty years in Scandanavia, the Adirondack Mountains of New York State and regions of Ontario adjacent to the Sudbury mining and smelting district. Recently Dillon et al. (1978) have reported that precipitation which is thirty to fifty times (pH 4.2-4.0) more acidic than normal (pH 5.7), is falling over extensive portions of central Ontario and it has been suggested that, as a result, some of Ontario's recreational lakes will be acidified. Evidence that this process is underway in south-central Ontario has been discussed by Scheider et al. (1978). The most visible and economically important result of lake acidification is the loss of viable fish populations.

The most important factor governing the sensitivity of fresh waters to the input of acidic precipitation is the geochemistry of the watershed. Geological terrain dominated by very insoluble silicate rocks and hence, having "soft-water" lakes is the most sensitive. Most of the Precambrian Shield located in northern and central Ontario is of this type although the highly variable glacial deposits in this area may be important in locally mediating the susceptibility to acid. Terrain south of the Shield is dominated by easily weathered carbonate rocks, and the hardwaters in this region are not threatened by acidification.

There is an urgent need for defining the areas of Ontario which have the greatest susceptibility for acidification. This information will allow a) a more quantitative assessment of the extent of potential lake acidification b) the prediction of acidification rates and c) the identification of the most threatened recreational lakes for consideration regarding the application of interim amelioration techniques to maintain existing fish populations. This manual outlines the rationale for parameter selection, and sampling and analytical methodologies for lake and stream surveys which will provide the best possible information for assessing acid susceptibility.

1.2 Parameters and Past Survey Information

The measure of the ability of a water to neutralize acid has been traditionally referred to as "total alkalinity". The analysis of total alkalinity involves the titration (Figure 1) of a known volume of sample

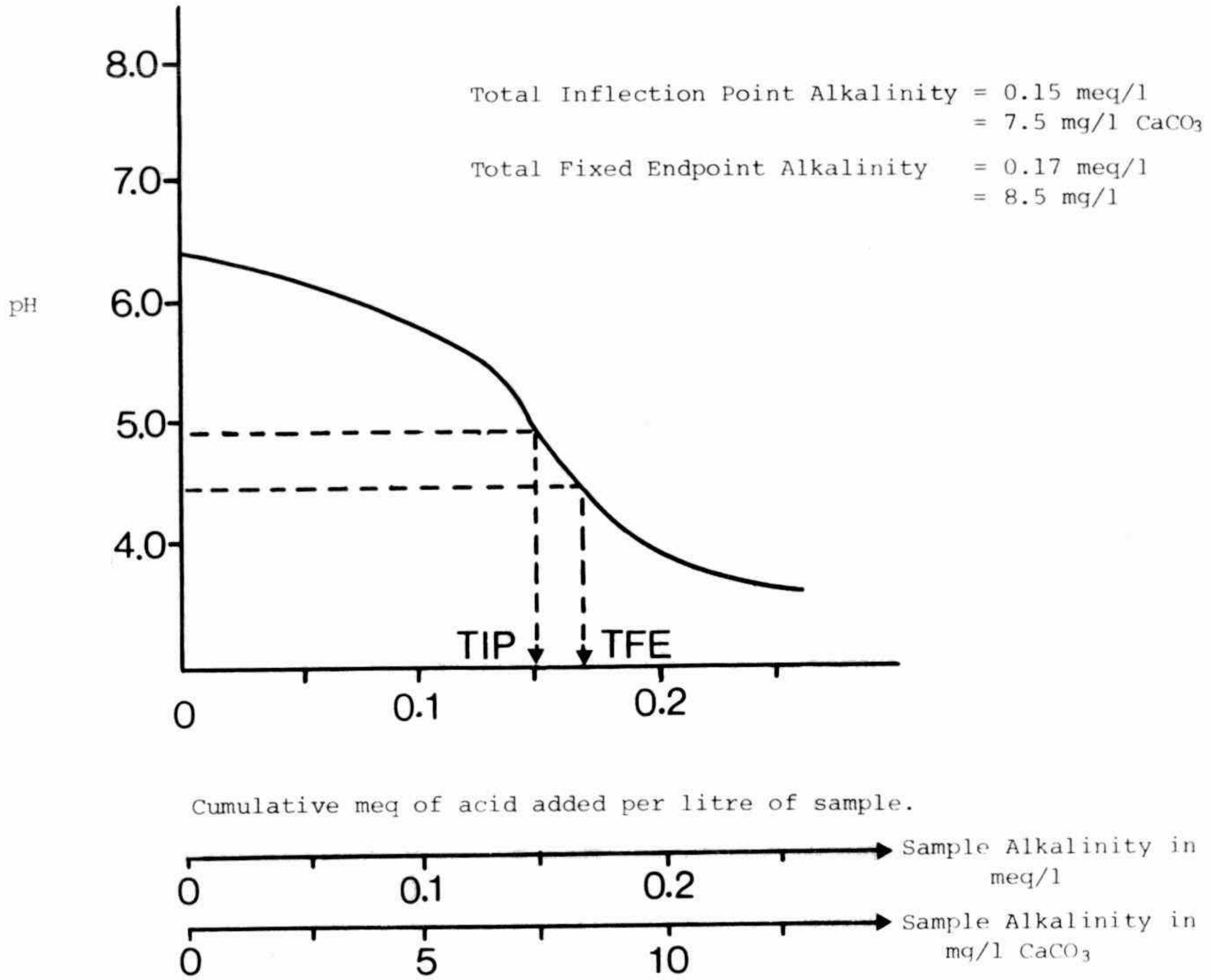

Figure 1: Hypothetical titration curve for a potentially acid susceptible lake sample. TIP Alkalinity value determined from amount of acid added to reach inflection point of curve (by Gran analysis). TFE Alkalinity value determined from amount of acid added to reach pH = 4.5.

with a standard acid to the pH corresponding to the equivalence point of the bicarbonate - carbonic acid reaction, i.e. the pH at which the concentrations of HCO_3^- and H_2CO_3 are equal.

$$HCO_3^- + H_3O^+ \rightarrow H_2CO_3 + H_2O \rightleftarrows CO_2 + 2H_2O$$

Below the equivalence pH, carbonic acid is in excess, no further reaction with hydrogen ion can occur, and the buffering capacity has been expended. This functional definition of alkalinity is based on the fact that the predominating buffering species in natural waters are carbonate and bicarbonate, particularly in "hard" waters, although in the extremely "soft" water lakes and streams found on the Canadian Shield, other buffering species (organics, particles, etc.) may be significant.

Ideally, the determination of total alkalinity requires that the inflection point of the titration curve be precisely located and the resultant value is called the "total inflection point alkalinity" (TIP). In practice, a pH of 4.5 is often assumed through the use of a bromcresol green-methyl orange endpoint indicator or a potentiometric titration to this specific pH. The alkalinity value derived in this manner will be called the "total fixed endpoint alkalinity" (TFE). For high alkalinity (hard water) samples, the TFE techniques yield reliable results (i.e. TFE≈TIP) but for low alkalinity samples, they over-estimate the true value since the inflection pH in these cases is nearer pH = 5.0 than 4.5.

Almost all past water quality surveys conducted on Precambrian Shield waters have employed a TFE method and hence, unrealistically high estimates of acid buffering capabilities will be drawn from the data. This fact is true no matter whether an extremely sensitive potentiometric TFE procedure was used or an insensitive field titration (indicator, eye dropper titrant addition, etc.) method was employed. The most appropriate use of the TFE alkalinity data obtained from past surveys is a) to define water systems which are not acid susceptible, b) to suggest where further sampling is warranted, and c) in the case of high quality potentiometric data, to infer relative levels of susceptibility for lakes in the 0-20 mg L^{-1} ($CaCO_3$) alkalinity range. The data base of "absolute" or correct water alkalinity values is very small; there is a great need for improving this situation as quickly as possible.

There are other parameters which indicate sensitivity to acid inputs. Specific conductivity (usually expressed in μmho cm^{-1} at $25^{0}C$) is a gross

indicator of the amount of dissolved ionic substances in a water sample, and due to the simplicity of its measurement, the accuracy of the historical data base is probably best for this parameter. Dilute water systems are the most susceptible, i.e. those with low conductivities. The predominant cationic species in Shield waters is usually Ca^{++} and a fairly direct relationship exists between calcium concentration and conductivity; thus, in the absence of conductivity data, calcium values may provide similar inferences. In some cases, the measurement of pH may also provide useful information although existing data is probably biased to high values because frequently only surface water samples were collected. The pH of these samples may reflect production in the upper strata.

Despite the limitations on historical alkalinity, conductivity, and pH data, it is possible to set values for any one of the parameters below which the water in question has a significant potential for acidification. These are as follows:

Alkalinity 15 mg L^{-1} $CaCO_3$ (0.3 meq L^{-1})

Conductivity 35 μmho/cm at $25^{o}C$

pH <6.0

These values may be used in an initial assessment of data to define which surface water system warrants further testing although there can be no guarantee that waters with values above these may not also be susceptible. This is particularly true if the data being considered are several years old.

Finally, elevated aluminum and manganese concentrations may indicate incipient acidification. These elements normally exist at low concentrations in unaffected, non-coloured surface waters (<50 μg L^{-1} for Al; <10 μg L^{-1} for Mn in aerobic waters), but concentrations up to one part per million (1000 μg L^{-1}) have been reported for lakes in Scandanavia and the Adirondack mountains of New York State. Measurements of these parameters in Ontario lakes are virtually non-existent.

1.3 Existing and Future Data Bases

As mentioned above, the existing data bases for assessing acidification potential are extremely limited in size and number. Efficient use of these and new data is primarily a function of the knowledge of their

existence. Mr. N. Conroy is maintaining a compilation of all scientists and groups who have existing data or are actively collecting them at present. The purpose of the list is to facilitate scientific collaboration between individuals with similar research interests as they relate to acidification problems. If you are engaged in such research and wish to be included in the list you are encouraged to contact Mr. Conroy at the following address:

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2.1 SAMPLING METHODS

The aim of any sampling endeavour is to obtain an aliquot which is as representative as possible of the whole system, or at least representative of a pre-defined portion of it. Collection of a lake surface water sample does not meet this criterion. A "profile" sample appropriate to the thermal conditions in the lakes is most desirable. In contrast, most of the streams on the Shield are small, unproductive, and well-mixed, so that it is feasible to collect a surface sample representative of the whole at that point in time.

There are several sampling methods which may be used in a survey of lakes carried out to define acidification potential. These will be discussed in order of desirability in the following sections along with suggestions for sample preservation.

2.2 Lake Sampling

a) Most Desirable Method - Volume Weighted Lake Composite (Specific details are outlined in Appendix 1).

The average whole-lake buffering capacity is best estimated by analyzing a volume-weighted composite sample. This sample is collected at 2 meter or smaller intervals at the deepest point in the lake. An amount from each stratum proportional to that stratum's volume is combined into a single sample. This sampling technique requires knowledge of the lake's morphometry but it does provide the most representative lake sample. Lake strata should be sampled at their midpoints using either a pump, Van Dorn, or Kemmerer sampler and the appropriate volume measured in a large graduated cylinder. The strata aliquots are then mixed in a clean plastic bucket or large glass or plastic bottle before appropriate sample bottles are filled.

b) Less Desirable Method - Non-weighted Lake Composite (Specific details are outlined in Appendix 2).

A reasonable estimate of buffering capacity may be determined from a sample which corresponds to a column of water through the epilimnion and metalimnion. The different chemical characteristics of each stratum are "averaged" to give a meaningful whole-lake datum.

The non-weighted lake composite sample may be most easily and accurately collected using a "tube" sampler, i.e. a piece of flexible plastic tubing weighted on one end and lowered through the water column to the bottom of the metalimnion or to one meter above the bottom in shallower lakes. It is necessary to determine the depth of the metalimnion using a temperature probe. This information may then be used to determine the length of tube needed to collect the sample. By pinching the tube at the surface, a discrete column of water may be retrieved and poured into a vessel (clean plastic bucket or large glass bottle) where mixing is facilitated prior to filling appropriate sample bottles. Retrieval may also be facilitated by tying a line to the weighted end of the tube and pulling it up "bottom end first". During the winter months when there is no stratification, a 5 meter tube sample taken through a hole in the ice should provide a satisfactory lake aliquot.

An alternative but less recommended approach is to take a series of Van Dorn or Kemmerer bottle samples at 2 meter intervals to the bottom of the metalimnion, pouring each in turn into a large mixing vessel until the profile sample is obtained. This method requires much more effort and time than the tube procedure, but yields a much larger sample volume.

c) Least Desirable Method - Discrete Layer Composite.

Collection of a Van Dorn or Kemmerer sample at the midpoint of each stratum followed by appropriate mixing is the least desirable method although it is still much better than the surface "grab" technique. It has the advantage that existing equipment may be utilized, but requires a prior measurement of the temperature profile of the lake in order to locate the three strata. In winter, a single sample 2-3 meters down will serve the same purpose.

d) Unacceptable Method - Surface Grab

For the reasons discussed previously, collection of a surface lake sample for assessing acid susceptibility is not recommended.

2.3 Sample Perishability

Alkalinity and pH both respond to dynamic changes occurring in the sample. If algal production proceeds in the closed sample then the pH will increase while the inorganic carbon levels will decrease. It is not possible to add any chemical preservative to the sample to stabilize either of these parameters, although filling the sample bottle right to the top (i.e. excluding air) prevents addition or loss of carbon dioxide by exchange with the atmosphere. The same is true for conductivity samples. It is essential that the integrity of the samples collected for alkalinity, pH and conductivity analysis be maintained as far as possible by keeping them cold and in the dark. This technique will minimize the changes which result from biological production. Use an ice chest for sample storage and transport between collection and analysis. If ice or "cold packs" are not available, some cold, hypolimnetic water may be used as a last resort. It is important to realize that keeping the samples in the cold and dark only minimizes the changes that can occur and should not be considered a substitute for conducting the appropriate analysis (see Section 3) as soon as possible after collection.

Samples collected for calcium, aluminum, and manganese analysis are less affected by biological processes; however, the latter two elements may be removed by chemical or surface reactions and hence the addition of ≈1 ml of nitric acid preservative per litre of sample is high recommended.

3.1 SAMPLE ANALYSES

As noted above, analyses of all perishable parameters should be conducted as soon as possible after sample collection. Field techniques for the analysis of alkalinity, pH and conductivity are discussed below. In contrast, samples for calcium, aluminum and manganese analysis are stable after appropriate preservation, and the low concentrations expected in lakes susceptible to acidification are best determined by sensitive techniques under controlled laboratory conditions.

3.2 Field Analysis of Alkalinity and pH (Specific details outlined in Appendix 3).

a) Most Desirable Method - Monitored Potentiometric Titration.

The true alkalinity (TIP) of the sample can only be obtained if a titration curve is obtained which may be analyzed mathematically to

determine the location of the inflection point. This may be achieved by titrating a known volume of sample (continuously mixed) with a standardized acid while continuously measuring the solution pH. The initial pH of the sample should be recorded before any acid titrant is added and since pH is a function of temperature the temperature of the sample should also be measured. Subsequently, the addition of each known aliquot of acid should be followed by a sufficient time interval to allow chemical equilibrium to be established, and the pH meter to reach a consistent reading. Record the pH value in each case. The volume of titrant addition must be known as accurately as possible. Use of high quality buret equipment (see Section 4) is a necessity. It is important that the number of additions be maximized in the pH range 5.5 to 3.5 to at least 20 points. The titration curve may be obtained by plotting cumulative acid added versus pH. The monitored titration should be performed as soon as possible after sample collection, perferably the same day or at least within twenty-four hours. With the proper equipment (discussed later) the titration may be conducted by field personnel, or alternatively, daily delivery of the samples to a field laboratory for analysis will allow more efficient data collection.

The location of the inflection point is determined later by either calculating the root of the second derivative function of the curve, or by calculating the intercept of the Gran function (F_1, discussed by Stumm and Morgan, 1970, p155-158) when plotted against cumulative acid added. The Gran technique is most commonly employed, and the calculations facilitated through the use of a programmable calculator. Calculation of the inflection point is most efficiently handled at a later date when a large number of titration curves can be analyzed together. Clearly this aspect of the alkalinity (TIP) determination is not a field activity and discussion of it will not be included here. Specific information on Gran plot or differential titration calculation can be obtained through the literature or by consultation with Ministry of the Environment staff (Laboratory Services Branch, Water Quality Section, P.O. Box 213, Rexdale, Ontario; Tel: (416) 248-3512).

In summary, the critical aspects of collecting and analyzing a water sample for pH and true alkalinity using the most desirable methods to define sensitivity to acidification are as follows:

i) collect a volume-weighted composite sample as per discussion in Section 2:2a and Appendix 1; collection of a "tube composite sample (Section 2:2b and Appendix 2) provides a reasonable although less representative sample.

ii) store the sample in clean (i.e. acid washed, rinsed at least four times with distilled water and at least two times with sample prior to being filled) glass or plastic bottles. Sample aliquots obtained for analysis of Ca, Mn, and Al should be stored in clean plastic bottles and acidified (1 ml nitric acid per litre).

iii) maintain the integrity of the sample (i.e. keep cold and in the dark) between collection and analysis.

iv) measure sample pH and conduct a monitored alkalinity titration using a pH meter and quality equipment for the addition of acid titrant.

v) when conducting the titration, maximize the number of data points (pH and titrant added) between pH 5.5 and 3.5

A minimum of twenty points is needed in this range.

vi) determine the TIP alkalinity later by using an appropriate mathematical method for locating the inflection point.

b) Less Desirable Method - High Precision TFE Alkalinity Titration

As noted earlier, the collection of TFE alkalinity data does not provide the absolute information needed to make an assessment of acidification susceptibility and thus for this purpose no method other than that discussed above is recommended. Nevertheless, high precision alkalinity results determined to an endpoint of pH = 4.5 using either a pH meter or indicator may be of value for comparative purposes. In order to obtain TFE data or sufficient precision to be worthwhile, similar titration equipment is needed as that used for the TIP analysis (excluding pH meter if indicator used). Hence there is little advantage in conducting a TFE analysis except for the time saving that may be obtained. The results obtained may be 2 to 5 times greater than the TIP value for low (<15 mg/l $CaCO_3$) alkalinity samples.

c) Unacceptable Method - Low Precision TFE Alkalinity Titration

Measurement of TFE alkalinity of acid susceptible waters using low precision equipment ("eye-dropper" burette, non-stirred titration vessel, etc.,) is not recommended under any circumstances.

3.3 Field Analysis of Conductivity (specific details outlined in Appendix 4).

Field conductivity is easily measured using a portable conductivity bridge, however, it is important that the temperature of the sample also be measured. Report conductivity values in μmhos cm^{-1} corrected to $25^{o}C$, or measured value and sample temperature.

4.1 EQUIPMENT

It is essential that good quality instruments be available for the measurement of pH, conductivity, and the performance of the alkalinity titration. Most commercially available field analysis kits are either incomplete or insensitive since they are usually designed for assessment of wastewaters or hard water systems.

Conductivity and pH may be accurately and easily measured using battery operated instruments. Even the titration may be similarly handled if simple stirring equipment is employed. Nevertheless it is possible to use "regular" laboratory equipment (i.e. requiring 115V power supply) if sample collection and analysis are arranged in consideration of this fact. High quality data can be obtained if sampling is conducted in the early day (with appropriate steps taken to ensure sample integrity) and is followed by analysis later on that same day.

The following equipment specifications should be considered as minimum requirements.

4.2 Specifications

a) pH Meter

- analog or digital output (digital outputs tend to foster fewer reading errors)
- relative accuracy ± 0.01 pH units

- temperature compensation
- repeatability ± 0.02 pH units
- optional considerations: expanded scale readout
  recorder output
  carrying case
  rechargeable batteries if battery operated
- probable cost - \$400 up
- electrodes: good quality gel filled pH-reference combination electrodes are the easiest to use and require the least maintenance, but standard glass pH and KCl reference electrodes are satisfactory (probable cost \$100 up).

b) Conductivity Meter

- multi-range readout
- accuracy ± 1% of range
- temperature compensation
- optional consideration: carrying case
  rechargeable batteries if battery operated
- probable cost \$250 up

c) Titration Equipment (not including standard glassware, support stands, supplies etc.)

i) stirring apparatus:
- capable of reproducible stirring
- commercially available stirrers usually employ a magnetic stirring bar and require line power
- simple "propellor" type stirrers may be simply built using battery operated motors such as those used in model boats or cocktail mixers

ii) buret:
- Class A, 10 ml glass buret readable to ± 0.02 ml is satisfactory but not recommended for field use due to its great fragility
- small volume reagent dispensing systems will have sufficient reproducibility (≈0.1%) to allow use as an acid buret

system; choose equipment capable of dispensing 0.1 - 0.5 ml aliquots and keep a count of "aliquots dispensed" to determine volume of acid added; probable cost $75 up.

-a micrometer syringe (2.0 - 2.5 ml) will provide a far greater degree of precision than the glass buret or dispenser; it will need appropriate support equipment (stands, clamps, etc.); probable cost $50 up (better syringe recommended).

d) Thermometer Probe (needed for "tube" sampling)

- response time <5 sec.
- working range 0-30^{o}C minimum; accuracy ± 1% of full scale or better
- portable; battery operated; rugged
- can use probe with long extension leads (at least 30m)
- direct reading (i.e. no bridge balancing or scale conversions).
- probable cost $200-$500 (with probe).

APPENDIX 1

Method for Volume-Weighted Composite Sampling

1) A knowledge of lake morphometry is necessary in order to determine the weighting which should be applied for each stratum. The volume weighting should be determined before any field activities are initiated. Once the surface areas enclosed by the depth contours have been determined (by planimeter or other means), the volumes of the intermediate strata may be calculated as follows:

$$Vx,y = \frac{y - x}{3} \left(Ay + Ax + (Ay\ Ax)^{\frac{1}{2}}\right)$$

where x = depth of the upper surface (plane) of the stratum
y = depth of the lower surface of the stratum
Ax = area of the upper surface (i.e. area enclosed by the x depth contour)
Ay = area of the lower surface
Vx, y = volume of the stratum between the x and y depths

The units of the above equation must be consistent (i.e. British or metric) and may be determined by the units of the available morphometry. The result is that the volume of each successively deeper stratum can be determined, down to the maximum depth of the lake. Normalize the strata volume ratio (e.g. $V_{Om,2m}$:$V_{2m,4m}$: $V_{4m,6m}$: etc) so that the sum of the volumes falls between 3000 and 4000, (to give total sample of 3000-4000 ml) and prepare a table of values (x, y stratum vs normalized volume) which can be taken to the sampling site.

2) Water should be collected from the mid-depth of each statum, e.g. at the 1, 3, 5 etc., meter depths for 2m intervals using either a pump sampler or a Van Dorn or Kemmerer sampler.

3) A volume of water (in milliliters) from each statum corresponding to the values found in the table produced above will be mixed to yield the volume-weighted sample. Measure the volume using a clean one litre graduated cylinder and pour the appropriate stratum aliquot into a clean plastic bucket or glass container. Rinse both the cylinder and bucket at least twice with a portion of the sub-sample from the surface stratum before measuring out the first stratum aliquot and placing it in the bucket.

4) Collect and measure the aliquot from each successively deeper stratum until the whole water column has been sampled. Mix the volume weighted sample in the bucket either by swirling or by stirring with a clean plastic spatula, and pour into appropriately cleaned and rinsed sample bottles. The total volume of sample obtained in this manner should equal the sum of the normalized values on the table, i.e. between 3 and 4 litres.

5) Samples collected for alkalinity analysis should be agitated as little as possible during the mixing procedure and should be stored in bottles that are filled to the top, i.e. with no air space.

6) Place the samples in a cooler which will a) keep them dark, and b) keep tham cold in summer and prevent them from freezing in winter.

7) As far as possible, minimize the length of time between sampling and analysis (<24 hours is considered optimum).

APPENDIX 2

Method for "Tube" Composite Sampling

1) Use flexible clear plastic tubing; before initial use, rinse the tube thoroughly with distilled water.

2) Use tubing sufficiently large to yield the necessary quantity of sample; for example, the volume of water collected in a tube of given internal diameter is as follows:

Tube I.D.	Total Sampling Depth	Approx. Volume
½" (12.7 mm)	12 meters	1500 ml.
	5 meters	630 ml.
¾" (19.1 mm)	12 meters	3400 ml.
	5 meters	1400 ml.
1" (25.4 mm)	12 meters	6100 ml.
	5 meters	2500 ml.

3) Weight one end of the tube and secure a line to the weight; this will facilitate retrieval.

4) When the lake is thermally stratified measure the depth-temperature profile of the lake using a thermistor probe. Ascertain the position of the bottom of the metalimnion by determining the depth (below the region of greatest temperature change) at which the observed temperature decrease is less than or equal to $1^{o}C$ per two meters. Lower the tube sampler through the water column to this depth or to one meter off bottom in shallower lakes. In winter, a five meter sampling depth may be used.

5) Pinch the tube off above the water surface so that, on retrieval, the composite sample remains in it.

6) Drain the sample into a clean plastic bucket or glass container, mix the sample and <u>discard entirely</u>. Repeat steps 4 and 5, and this time, once the sample has been drained into the bucket, mix it thoroughly (either by swirling or by stirring with a clean plastic spatula) and pour into appropriately cleaned sample bottles.

7) Samples collected for alkalinity analysis should encounter as little splashing as possible during the mixing procedure and should be stored in bottles that are filled to the top, i.e. with no air space.

8) Place the samples in a cooler which will a) keep them dark, and b) keep them cold in summer or prevent them from freezing in the winter.

9) As far as possible, minimize the length of time between sampling and analysis (<24 hours is considered optimum).

APPENDIX 3

Methods for the Analysis of pH and Alkalinity

1) The following methods for pH and alkalinity analysis require the presence of a properly standardized pH meter; accurate standardization is of critical importance.

2) pH Meter Standardization

a) The pH meter should be standardized using a buffer solution near the pH of the sample and the calibration checked with a buffer which has a pH below the expected inflection point value.

b) Buffers and samples should be at the same temperature.

c) Measure the temperature of the samples and set the temperature compensation dial on the pH meter to this value.

d) Various commercially available buffers may be used. The two buffers discussed here are usually sold as "pH = 6.87" (25^{o}C; a solution of 0.025 M KH_2PO_4 and 0.025 M Na_2HPO_4) and "pH = 4.01" (25^{o}C; a solution of 0.05 M $KHC_8O_4H_4$, i.e. phthalate).

These nominal pH values are for the solutions at 25^{o}C; however since the solution pH changes with temperature, and the samples will be colder than this, the pH meter calibration value must be adjusted accordingly. Standard pH values as functionsof temperature for the two buffers mentioned above are as follows:

Temperature (^{o}C)	"pH = 6.87" Buffer	"pH = 4.01" Buffer
0	6.984	4.003
5	6.951	3.999
10	6.923	3.998
15	6.900	3.999
20	6.881	4.002
25	6.865	4.008
30	6.853	4.015

Source: Handbook of Chemistry and Physics, Chemical Rubber Co., 57th Ed.

Standardize the pH meter by placing the electrodes into a beaker containing a "pH = 6.87" buffer and setting the reading on the meter (using the calibration control) to the value appropriate to the buffer/sample temperature given in the table above. Make sure that the buffer is being stirred in the same way as the samples will be during the titration.

e) Remove the "pH = 6.87" buffer, rinse the electrodes with distilled water, and substitute the "pH = 4.01" buffer. If the temperature compensator is correctly set and standardization is also correct, the pH value of this second buffer should be within 0.02 units from the expected value, probably within 0.01 units. If this is not the case, re-calibrate by adjusting the temperature compensator, not the calibration control.

f) When using the pH meter, always rinse the electrodes with distilled water between solutions and never let the electrodes "dry out".

3) Analysis of Sample pH

a) Rinse a pipet with sample, and then pipet a 50 or 100 ml aliquot into an appropriate, clean beaker. Never use a beaker that previously contained a buffer.

b) Place the pH electrodes in the sample and after allowing the system to come to equilibrium, record the sample pH.

4) Alkalinity Titration

a) Arrange the electrodes, stirrer, and buret to facilitate titrant addition and pH measurement.

b) Use previously standardized sulphuric or hydrochloric acid. The acid strength used will depend on the sample volume selected and the type of buret equipment used. A small volume, high precision buret (e.g. micrometer syringe) will allow the use of a comparatively strong acid, say 0.0200 N, and the volume used will probably be less than 2.5 ml for a 100 ml sample. A reagent dispenser system, dispensing 0.1 ml aliquots will give reliable results if a more dilute acid is employed (i.e. 0.0100 N).

c) Make additions of acid, to the continuously stirred sample, allow the pH reading to stabilize and record the cumulative amount of acid added and the equilibrium pH. Ensure that no acid remains attached to the tip of the buret which would give an incorrect value for the amount of acid added; the tip of the micrometer syringe may be immersed in the sample to eliminate this problem.

d) Maximize the number of readings taken between pH 5.5 and 3.5

e) Stop the titration when pH = 3.5 is reached.

f) It is recommended that all titration results be recorded and kept in a book which will facilitate later inflection point determination. One or two initial "practice" titrations are advised in order that the analyst may become familiar with the idiosyncracies of his titration system.

APPENDIX 4

Method for the Analysis of Conductivity

1) Conductivity meters measure the electrical resistance offered by a water sample between two platinum electrodes in some kind of cell assembly. The conductivity measured is a function of the cell constant (usually pre-determined by the manufacturer) and temperature.

2) It is common practice to report all conductivity values corrected to 25°C, and hence most new conductivity meters contain an automatic temperature compensator. Older meters may not have a compensator and both sample temperature and conductivity values must be recorded. and the corrected value calculated. It is good practice to record sample temperature in any case.

3) Follow the simple instructions that come with the meter; be sure to rinse the cell two or three times with sample before taking the conductivity reading.

4) The accuracy of the meter may be checked with conductivity standards; a 0.0005 M KCI solution has a specific conductance of 73.9 μmho/cm (25°C) while a 0.005 M KCI solution has a value of 718 μmho/cm (25°C)

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